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(54) Title: JET INK COMPOSITION

(57) Abstract

The present invention provides a jet ink composition having short drying times and suitable for printing on food and pharmaceutical articles comprising a first organic solvent, a first binder resin, and a surface modified or coated colorant. The first binder resin is selected from the group consisting of shellac and polyvinylpyrrolidone. The first organic solvent is preferably ethanol. The jet ink composition may further comprise water, a pH adjusting agent such as ammonium hydroxide, and other additives. The surface modified or coated colorant comprises an inorganic colorant such as titanium dioxide, a second organic solvent such as ethanol, and one or more second binder resins selected from the group consisting of shellac, polyvinylpyrrolidone, and cellulose ethers such as methylcellulose and ethycellulose. The present invention also provides an improved method of jet printing whereby short drying times and high print quality are achieved, the improvement comprising using the jet ink composition of the present invention. The jet ink composition of the present invention is particularly suitable for use on glazed candies.

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# JET INK COMPOSITION

The present invention relates to jet ink compositions in general, and to food grade jet ink compositions in particular. The jet ink compositions of the present invention are suitable for jet printing on food and pharmaceutical articles such as candies and tablets.

Ink jet printing is a well-known technique by which printing is accomplished without contact between the printing device and the substrate on which the printed characters are deposited. Briefly described, ink jet printing involves the technique of projecting a stream of ink droplets to a surface and controlling the direction of the stream electronically so that the droplets are caused to form the desired printed message on that surface.

The technique of jet ink printing or non-contact printing is particularly well suited for application of characters onto food and pharmaceutical articles, including, for example, tablets, pills, pellets, suppositories, and candies. The jet printing method is considered superior to impact printing methods such as stamping which tends to damage the articles.

Reviews of various aspects of ink jet printing can be found in these publications: Kuhn et al., *Scientific American*, April, 1979, 162-178; and Keeling, *Phys. Technol., 12(5)*, 196-303 (1981). Various ink jet apparatuses are described in the following U.S. patents: 3,060,429, 3,298,030, 3,373,437, 3,416,153, and 3,673,601.

In general, a jet ink composition must meet certain rigid requirements to be useful in ink jet printing operations. These relate to viscosity, resistivity, solubility, compatibility of components and wettability of the substrate. Further, the jet ink must be quick-drying and smear resistant, resist rubbing, and be capable of passing through the jet nozzle without clogging or drying, and permit rapid cleanup of the machine components with minimum effort.

In recent years there has been significant

developmental activity in the area of ink compositions suitable for ink jet printing, and several jet ink compositions are known. Some examples of known inks are set forth below.

UK patent application Serial No. GB 2,105,735 reportedly discloses a jet ink composition comprising an oil soluble dye-impregnated polyurethane latex dispersed in an aqueous medium.

U.S. Patent 4,155,768 reportedly discloses a jet ink which contains a water soluble dye and a polyamine containing 6 or fewer nitrogen atoms per molecule, with the ink having a pH of 8 or below.

U.S. Patent 4,197,135 reportedly discloses a jet ink which contains a water soluble dye and a polyamine containing 7 or more nitrogen atoms per molecule, with the ink composition having a pH of 8 or above.

U.S. Patent 4,680,332 reportedly discloses a jet ink composition comprising a water insoluble polymer such as a polyacrylate dispersed in a liquid medium, the polymer containing therein an oil soluble dye, and a nonionic stabilizer permanently attached thereto.

U.S. Patent 4,692,188 reportedly discloses a process for the preparation of jet ink compositions, comprising (1) dissolving in a water-immiscible organic solvent a polymer composition and an organic oil soluble dye; (2) adding an aqueous phase water-surfactant mixture thereto; (3) affecting emulsification thereof; and (4) subsequently evaporating from the emulsion the solvent thereby resulting in an ink with the dye trapped in the polymer particles suspended in the aqueous phase. The polymer compositions include polycarbonates, polystyrene, polymethacrylates and copolymers thereof.

U.S. Patent 5,080,716 reportedly discloses a jet ink composition comprising a recording agent, a liquid medium capable of dissolving or dispersing the recording agent, and a substituted benzene or toluene sulfonamide compound.

U.S. Patent 5,098,475 reportedly discloses a jet ink

composition comprising a solution with a dendrimer coloured with a dye or dyes covalently attached thereto.

U.S. Patent 5,100,470 reportedly discloses an ink jet ink comprising a water soluble dye, water with or without a water soluble organic solvent, and sufficient polyalkylene polyamine to provide the ink with a pH of at least 9.

U.S. Patent 5,120,361 reportedly discloses an aqueous jet ink composition comprised of a dendrimer, and a dye.

U.S. Patent 5,131,949 reportedly discloses a jet ink composition including a recording agent, a liquid medium capable of dissolving or dispersing the recording agent, and a compound having an amide group.

U.S. Patent 5,207,825 reportedly discloses a jet ink composition which comprises an aqueous liquid vehicle, a colorant, and a polymeric additive which is a substituted bisphenol A derivative.

U.S. Patent 5,213,613 reportedly discloses a jet ink comprising a recording agent and a liquid medium capable of dissolving or dispersing the recording agent therein, wherein the ink contains an imide compound and at least one compound selected from the group consisting of urea, thiourea and derivatives thereof, and volatile alkaline compounds.

U.S. Patents 5,215,577 and 5,178,671 reportedly disclose jet ink compositions comprising a recording agent and a liquid medium for dissolution or dispersion thereof, the recording agent being an aromatic sulfonated diazo compound.

U.S. Patent 5,254,158 reportedly discloses a jet ink composition which comprises an aqueous liquid vehicle, a colorant, and an additive selected from the group consisting of amine alkoxylates, sorbitan monoester alkoxylates, alkylene oxide adducts of glycerin, and mixtures thereof.

U.S. Patent 5,254,159 reportedly discloses a jet ink composition comprising water, an anionic dye, and a polyamine such as N,N'-bis(3-aminopropyl)-1,2-

ethylenediamine or a dendrimer.

U.S. Patent 5,256,193 reportedly discloses an aqueous jet ink composition comprised of a dendrimer, and a dye comprised of a porphyrin chromophore.

U.S. Patent 5,266,106 reportedly discloses an aqueous jet ink composition comprised of a dye and a grafted dendrimer such as a dendrimer grafted with a nonionic alkylene oxide oligomer.

U.S. patent application Serial No. 08/502,330, filed July 13, 1995, discloses certain jet ink compositions comprising a polyamine such as a dendrimer, a colorant, and an acidic resin, and suitable for printing on glass and other surfaces.

U.S. patent application Serial No. 08/317,339, filed October 4, 1994, discloses certain jet ink compositions suitable for ink jet printing on food items comprising water, a colorant, and a binder resin. The ink composition is prepared by mixing together the water, a binder resin such as shellac or polyvinylpyrrolidone, a colorant such as titanium dioxide, and other additives such as humectants and pH adjusting agents. The jet printed messages however take a relatively long time, nearly 2 minutes to dry when printed on glazes candies, due to the presence of a significantly large amount of water in the ink composition. In many instances, food articles such as candies have a glaze or coating on the surface. For instance, M&M candies are coated with a shellac glaze.

Commercially available food grade jet ink compositions generally are composed of a colorant in a water base. Several of these ink compositions have the disadvantage of poor readability when printed on dark coloured substrates such as candies. These ink compositions have the additional disadvantage that they dry very slowly, especially when printed on glazed candies such as shellac glazed candies. Long drying times reduce productivity and adversely affect the print quality due to the possibility of smudging.

Thus there exists a need for jet ink compositions that

are suitable for use on food, pharmaceuticals, and other edible or ingestible materials. There exists a need for ink jet ink compositions suitable for jet printing on coated or glazed candies.

Further, there exists a need for jet ink compositions that are easy to prepare and are stable without undergoing phase separation. There exists a need for ink jet ink compositions that dry fast and dry without smearing the print. There exists a need for ink jet ink compositions that offer increased line speed and allow printing large amount of information. There exists a need for ink jet ink compositions containing agents that provide improved film forming ability.

The present invention provides jet ink compositions suitable for use on food, pharmaceuticals, and other edible or ingestible materials, especially on coated and glazed candies.

The present invention provides a jet ink composition having short drying times comprising a surface modified or coated colorant, an organic solvent, and a first binder resin. The first binder resin is selected from the group consisting of shellac and polyvinylpyrrolidone. The first organic solvent is preferably ethanol. The jet ink composition may further comprise water, a pH adjusting agent such as ammonium hydroxide, and other additives. The surface modified or coated colorant comprises a colorant particle of size in the range of from about 0.01 microns to about 100 microns, an organic solvent, and an anchoring agent.

The present invention provides jet ink compositions having short drying times that are suitable for printing on food and pharmaceutical articles, such as candies, tablets, and pills. The jet ink composition of the present invention comprises a surface modified or coated colorant, an organic solvent, and a first binder resin. The organic solvent being volatile provides short ink drying times.

It has been found that the jet ink composition of the present invention can be advantageously prepared by first

preparing a surface modified or coated colorant and then preparing the inventive jet ink composition using the surface modified or coated colorant. When the ink composition is prepared using the surface modified or coated colorant, the ink composition has greater stability and uniformity than an ink composition prepared by mixing in one step the unmodified or uncoated colorant and the other ingredients including anchoring agent, binder resin, and solvents.

The jet ink composition of the present invention, in general, exhibits the following characteristics for use in ink jet printing systems: (1) a viscosity of from about 3 centipoises (cps) to about 5 cps at 25°C; (2) an electrical resistivity of from about 1000 ohm-cm to about 1800 ohm-cm; and (3) a sonic velocity of from about 1500 meters/second to about 1700 meters/second.

In addition, for use on food and pharmaceutical articles, the ingredients chosen should use Generally Recognized as Safe (GRAS) ingredients as listed in 21 C.F.R. Sections 73, 173 and 184.

The drying times of the jet ink of the present invention are below 2 minutes, preferably below about 30 seconds, and more preferably below about 10 seconds.

A detailed discussion of each of the ingredients and a method of preparation of the jet ink composition of the present invention are set forth below.

SURFACE MODIFIED OR COATED COLORANT

The preparation of the surface modified or coated colorant is disclosed in detail in the concurrently filed U.S. patent application, entitled "Surface Modified or Coated Colorants" (Zou et al.). The surface modified or coated colorant comprises a suitable colorant, one or more second binder resins, and an organic solvent. Examples of colorants suitable for human or animal consumption include any colorant approved by the FDA and meeting the specifications outlines in the Code of Federal Regulations, Title 21, Parts 73.575, 73.1575, and 73.2575, including

titanium dioxide, synthetic iron oxide, alumina, ferric ammonium citrate, calcium carbonate, ferric ammonium ferrocyanide, ferric ferrocyanide, chromium oxide and chromium hydroxide greens, mica, talc, and zinc oxide.

The colorant can have any suitable particle size, for instance, the particle size can range from about 0.01 microns to about 100 microns. It is preferred for use in ink jet printing purposes that the mean particle size is in the range of from about 0.01 microns to about 25 microns, more preferably from about 0.01 microns to about 5 microns, and even more preferably from about 0.01 microns to about 2 microns.

A preferred colorant is titanium dioxide. Any suitable titanium dioxide, anatase or rutile, can be employed. Any suitable titanium dioxide that is commercially available can be employed. KOWET™ brand titanium dioxide is an example of a suitable commercially available titanium dioxide. It is a dense, white, water insoluble powder, has the anatase crystal structure and a particle size of 0.3 microns mean and 1.0 microns maximum. KOWET brand titanium dioxide is available from Werner-Jenkinson Co. in St. Louis, Missouri.

Any suitable amount of the colorant can be used in the preparation of the surface modified or coated colorant. The colorant is present preferably in the range of from about 10% to about 70% by weight of the surface modified or coated colorant, more preferably in the range of from about 20% to about 60% by weight of the surface modified or coated colorant.

Any suitable solvent known to those of ordinary skill in the art can be used to prepare the surface modified or coated colorant. The solvent should have sufficient solubility for the anchoring agent and the binder resin. The solvent is preferably organic and has a low viscosity so as to allow easy mixing of the various components of the surface modified or coated colorant. Examples of suitable solvents include alcohols, ketones, and esters.

When the surface modified or coated colorant is to be

used for human or animal consumption, care should be taken by selecting solvents which are safe for consumption. Any solvent approved by the FDA for this purpose can be used. Examples of suitable solvents include ethanol, isopropanol, n-butyl alcohol, methylene chloride, acetone, ethylacetate, and cyclohexane, and the like. Ethanol is a preferred solvent. Denatured ethanol of 190 proof and pure ethanol of 200 proof are further preferred.

Any suitable amount of the solvent can be used in the preparation of the surface modified or coated colorant. The solvent is present preferably in the range of from about 10% to about 80% by weight of the surface modified or coated colorant, and more preferably in the range of from about 20% to about 60% by weight of the surface modified or coated colorant.

The surface modified or coated colorant comprises a second binder resin, preferably a shellac anchoring agent which adheres to the colorant particles. It is preferred that the agent is capable of forming a film or coating on the surface of the colorant particle, and it is further preferred that the agent forms a continuous film on the surface of the colorant particle.

Shellac has been known to man as a resinous coating material for a long time. Shellac, as the word is known and used today, refers to all forms of purified lac. Lac is the hardened resinous secretion of the tiny scale insect, *Laccifer lacca* (Kerr) of the super family Coccidae. The shellac may be of the hand-made, machine-made, or the bleached type.

Shellac contains only carbon, hydrogen, oxygen, and a negligible amount of ash. Elementary analysis yields carbon, 67.9%, hydrogen, 9.1%, and oxygen, 23.0%, which gives an empirical formula $C_4H_6O$. The molecular weight is about 1000. Using this molecular weight, an average shellac can be assigned a formula of $C_{60}H_{90}O_{15}$, and from its acid, saponification, and hydroxyl values, the molecule has been reported to contain one free acid group, three ester linkages, and five hydroxyl groups. There is evidence that

it contains a free or potential carbonyl group. It is an acid resin with an ionization constant $K = 1.8x10^{-3}$. It is also known that at least one of the constituents of shellac has one unsaturated linkage (-C=C-).

The saponification value of bleached shellac is in the range of 230-260 mg KOH/g, the acid value is in the range of 73-95 mg KOH/g, the ester value is in the range of 150-180 mg KOH/g, the hydroxyl value is in the range of 230-260 mg KOH/g, and the iodine value is in the range of 7-12 decigram I/g.

Any suitable shellac can be used. It is preferred that a "refined" bleached shellac is used to prepare the ink concentrate of the present invention. "Refined" refers to the removal of the natural shellac wax, and thus a refined bleached shellac may have a low wax content of about 0.1-0.2% by weight, whereas a "regular" or unrefined bleached shellac may have a wax content of 4.0-5.5% by weight.

Any suitable commercially available shellac can be used to prepare the surface modified or coated colorant. An example of a suitable refined bleached shellac is the Certified R-49 Refined Bleached Shellac available from Montrose-Bradshaw-Zinsser Group in Westport, Connecticut. The above shellac is a free flowing, pale yellow, granular powder having an acid number of 91.0 mg KOH/g maximum, an ash content of 0.5% maximum, alcohol insolubles content of 0.2% maximum, total chlorides content of 0.2% maximum, free chlorides content of 0.1% maximum, a moisture content of 6.0% maximum, a wax content of 0.2% maximum, and a colour rating (35% NV in alcohol) of 6 Gardner Standards maximum.

Any suitable amount of shellac can be used in the preparation of the surface modified or coated colorant. Shellac is present preferably in the range of from about 5% to about 35% by weight of the surface modified or coated colorant, and more preferably in the range of from about 10% to about 25% by weight of the surface modified or coated colorant.

The exact mechanism(s) by which shellac interacts with

the colorant to provide the surface modified or coated colorant has not been established. While intending not to be held to any particular theory or mechanism, the following is offered as a possible mechanism.

Commercial titanium dioxide usually contains some surface modifications. Thus, $TiO_2$ is modified with silica, alumina, or other materials such as phosphates, zinc oxide, and precipitated titania and organic coatings. These surface modifications are thought to be responsible for many of the surface characteristics of $TiO_2$. For instance, organics are reported to adsorb on $TiO_2$ surfaces, and the adsorption is in patches or on sites on $TiO_2$ surfaces rather than adsorbing uniformly. The number of active sites is estimated at about $10^8/cm^2$. These active sites are of distinctive types and each type of active site adsorbs one type of polar group.

It is believed that in the surface modified or coated colorant, the colorant surface is surrounded by the shellac molecules. The hydroxyl, carboxyl, and ester groups of shellac are adsorbed, anchored, or bonded with the active sites of the hydrophilic surface of titanium dioxide. The excess of free hydroxyl, carboxyl, and carboxylic ester groups present in the shellac molecules may react with one another to produce a film around the surface of the titanium dioxide particle. The inter- and intra-esterification and/or transesterification may further cause the thermal polymerization of the shellac molecules. It is believed that the foregoing reactions may produce a film around the surface of the titanium dioxide particle. The excess free hydroxyl, carboxyl, and carboxylic ester groups may in addition, interact with the organic solvent, for instance, with the hydroxyl group of alcohol by hydrogen bonding and by esterification. The hydrogen bonding solvent will solvate the shellac molecules and prevent the formation of shellac aggregates. The interaction between shellac and the solvent may be further responsible for the good dispersibility of the surface modified or coated colorant, for instance in dispersing in the ink medium.

When binder resins are also employed to modify or coat the particle surface, it is believed that the shellac molecules interact with the binder resins to yield optimal surface modification or coating.

The surface modified or coated colorant may include more than one binder resin which act in various ways to optimize the surface properties of the colorant. For instance, the binder resins may interact to provide stability to the film formed on the surface of the colorant. The binder resins may act as a film plasticizer. The binder resins may also help in forming a good stable suspension of the surface modified or coated colorant when the latter is employed to prepare, for instance, an ink composition.

Any suitable second binder resin can be employed in the preparation of the surface modified or coated colorant. Examples of suitable binder resins include shellac, polyvinylpyrrolidone (PVP), polyvinylpyridine, polyamide polymers of linoleic acid with polyamines such as di, tri- and tetra- ethylene triamine, poly(N-vinyllactam) wherein the lactam is a 5, 6, or 7 membered ring, polyvinylalcohol, vinylalcohol/vinylacetate copolymers, N-vinyllactam/ vinylacetate copolymers wherein the lactam is a 5, 6, or 7 membered ring, vinylpyrrolidone-vinylacetate copolymers, cellulose ethers such as methylcellulose, ethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose, and sodium carboxymethylcellulose, cellulose esters such as cellulose acetate and cellulose acetate propionate, lecithin, arabic, karaya, tragacanth, xanthan, and alginate type gums, and the like.

Shellac, PVP and ethylcellulose are preferred examples of binder resins for preparing the surface modified or coated colorant, especially where $TiO_2$ is the colorant. Any suitable PVP or ethylcellulose can be used. PVP can be prepared by the polymerization of N-vinylpryrrolidone monomer by methods known to those of ordinary skill in the art, including free radical or redox polymerization

methods. An example of a suitable commercially available PVP is the POVIDONE™ USP grade PVP, sold as PLASDONE™ brand PVP by GAF Chemicals Corp. in Wayne, New Jersey. PLASDONE PVP is available in several types, ranging in molecular weight from about 8,000 to about 1,200,000 Daltons, including the K-25, K-26/28, K-29/32, C-15, C-30, and K-90 types. K values of K-25, K-26/28, K-29/32, C-15, C-30, and K-90, are respectively, 25, 26-28, 29-32, 15, 30, and 90. The C grade PVP is pyrogen-free. The K-value is related to the intrinsic viscosity [η] and molecular weight of the polymer by the following expressions:

$$[\eta] = 2.303\ (0.001\ K + 0.000075\ K^2)$$

$$[\eta] = kMv^a,$$

where Mv is the viscosity average molecular weight, k = $1.4 \times 10^{-4}$, and a = 0.7.

All of the above types of PVP can be suitably employed to prepare the surface modified or coated colorant of the present invention. PVP of viscosity average molecular weight in the range of about 20,000 to 50,000 Daltons is preferred. K-29/32 is a preferred PVP, having a viscosity average molecular weight of approximately 38,000 Daltons.

Ethylcellulose can be prepared by any method known to those of ordinary skill in the art, including by the reaction of ethyl chloride with alkali treated cellulose. Ethylcellulose is commercially available from Dow Chemical Co. in Midland, Michigan, as ETHOCEL™, in several grades. The ethoxyl content of ethylcellulose ranges from 45.0% to 52.0% by weight of ethylcellulose. The most common ones have an ethoxyl content of 45.0% to 49.5%, corresponding to the degree of substitution of 2.25 to 2.58 ethoxy groups per anhydroglucose unit. The "Standard" grade ETHOCEL has an ethoxyl content of 48.0% to 49.5%, and the "Medium" grade ETHOCEL has an ethoxyl content of 45.0% to 47.0% by weight of ethylcellulose. The ETHOCELs are available in a variety of molecular weights as reflected by the various viscosities of the polymers which range from about 3 to about 220 centipoises (cps) when measured as follows. The

viscosity was measured as 5% solutions at 25°C in an Ubbelohde viscometer, in a solvent of 60% toluene and 40% ethanol for Medium products, and in a solvent of 80% toluene and 20% ethanol for Standard products. Thus, Standard #4 has a viscosity of 3-5.5 cps, Standard #7 has a viscosity of 6-8 cps, Standard #10 has a viscosity of 9-11 cps, Standard #20 has a viscosity of 18-22 cps, and Standard #45 has a viscosity of 41-49 cps, and Medium #50 has a viscosity of 45-55 cps, Medium #70 has a viscosity of 63-85 cps, Medium #100 has a viscosity of 90-110 cps. Standard #4 ETHOCEL is a preferred ethylcellulose binder resin for the preparation of the surface modified or coated colorant, especially the ink concentrate of the present invention. Several of the above ETHOCELs are available in Premium and Industrial grades. The Premium grade is further preferred. Thus, Standard #4 - Premium is a further preferred binder resin.

Any suitable amount of the second binder resin can be used in the preparation of the surface modified or coated colorant. The binder resin is preferably present in the range of from above 0% to about 35% by weight of the surface modified or coated colorant, more preferably in the range of from about 2% to about 20% by weight of the surface modified or coated colorant.

More than one binder resin can be used to prepare the surface modified or coated colorant. Thus, PVP and ethylcellulose can be used together as the binder resin. Thus, it has been found to be advantageous to use PVP, ethylcellulose and shellac to prepare the surface modified or coated colorant useful as the ink concentrate of the jet ink suitable for marking food and pharmaceutical items.

Any suitable combination of PVP and ethylcellulose binder resins can be used in the preparation of the surface modified or coated colorant. The PVP binder resin is preferably present in the range of from above 0% to about 20% by weight of the surface modified or coated colorant, and more preferably in the range of from about 2% to about 15% by weight of the surface modified or coated colorant.

The ethylcellulose binder resin is preferably present in the range of from above 0% to about 15% by weight of the surface modified or coated colorant, and more preferably in the range of from about 2% to about 10% by weight of the surface modified or coated colorant.

The surface modified or coated colorant can be prepared by any suitable methods known to those of ordinary skill in the art. For instance, the shellac anchoring agent can be first dissolved in the solvent at a suitable temperature to bring about rapid dissolution. The temperature of mixing is generally in the range of from about 20°C to about 60°C, and preferably in the range of from about 35°C to 45°C. Another desired second binder resin can then be added to the solution and mixed.

When the dissolution of the binder resins is complete, the solution is preferably mixed for another 5-10 minutes at an increased speed, preferably at a speed in the range of from about 800 rpm to 1200 rpm. A suitable amount of the colorant is then added slowly to the above solution. After the addition of the colorant is complete, the mixing speed is increased, preferably to about 4,000 rpm to about 5,000 rpm. The mixing is continued for a suitable period of time to obtain a smooth, uniformly mixed paste, preferably for a period of from about 20 minutes to about 40 minutes.

The above paste can be suitably diluted with a solvent and ground in a suitable mill such as ball mill. The ball milling operation assists in breaking up of any agglomerates and in producing a narrow particle size distribution of the surface modified or coated colorant.

Any suitable ball mill can be employed. For instance, a bill mill containing YTZ (yttria stabilized zirconia) beads of the diameter in the range of from about 0.4 mm to about 0.8 mm can be employed.

The surface modified or coated colorant prepared as above can be further dried to remove any free organic solvent. For instance, free ethanol may be removed by any suitable means, preferably by under vacuum or under flowing

air or nitrogen. The drying is preferably carried out at ambient temperature or below.

The surface modified or coated colorant such as the surface modified or coated titanium dioxide is valuable as ink concentrate for various reasons including the small particle size and narrow particle size distribution, and offers great opportunity for preparing pigmented white jet inks which are sedimentation free and safe for human consumption.

Any suitable amount of the surface modified or coated colorant can be used to prepare the jet ink composition of the present invention. The surface modified or coated colorant is present preferably in the range of from about 10% to about 30% by weight of the jet ink composition, and more preferably in the range of from about 16% to about 25% by weight of the jet ink composition. Excessive amounts of the surface modified or coated colorant would adversely affect the print quality.

INK SOLVENT

The jet ink composition of the present invention is prepared in a suitable ink solvent. An organic solvent is preferred. Any suitable organic solvent can be used to prepare the inventive jet ink composition. An organic solvent having low boiling point is further preferred. Examples of suitable organic solvents include ethanol, iso-propanol, n-butanol, ethylacetate and the like. If desired, mixtures of solvents can be used. The jet ink composition of the present invention may contain water in addition to the aforesaid solvents. Thus, a mixture of ethanol and water can be used. Any suitable combination of solvent and water can be employed. It is preferable to use minor amounts of water. Excessive amounts of water will affect the stability of the jet ink composition and the ink drying times.

Any suitable amount of the ink solvent can be used in the preparation of the inventive surface jet ink composition. The solvent is present preferably in the

range of from about 40% to about 90% by weight of the jet ink composition, and more preferably in the range of from about 50% to about 80% by weight of the jet ink composition. When water is used, the amount of water is preferably below 15% by weight of the jet ink composition, and more preferably in the range of from about 8% to about 12% by weight of the jet ink composition. To eliminate any confusion, the ink solvent is also referred to herein as the first organic solvent to distinguish it from the second organic solvent used to prepare the surface modified or coated colorant.

INK BINDER RESIN

The jet ink composition of the present invention further comprises an ink binder resin. Any suitable binder resin can be used. Examples of binder resins suitable for food and pharmaceutical applications include shellac, polyvinylpyrrolidone (PVP), cellulose ethers such as methylcellulose, ethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose, and sodium carboxymethylcellulose, cellulose esters such as cellulose acetate and cellulose acetate propionate, lecithin, arabic, karaya, tragacanth, xanthan, and alginate type gums, and the like. Shellac and PVP are examples of preferred binder resins. Any of the shellac and PVP materials described earlier can be used to prepare the inventive jet ink composition. Shellac is also commercially available as solutions in ethanol. These solutions are available as 2, 3, 4, 5, 6, 7, or 8 pound cut. The 4 pound cut solution, for instance, contains 1,216 grams of shellac in 1 gallon of SDA-45 200 Proof ethyl alcohol.

Any suitable amount of the ink binder resin can be used in the preparation of the jet ink composition of the present invention. The ink binder resin is preferably present in the range of from above 0% to about 25% by weight of the jet ink composition, more preferably in the range of from about 1% to about 15% by weight of the jet

ink composition. The amount of binder resin set forth in this paragraph does not include the amount of binder resin used to prepare the surface modified or coated colorant set forth earlier.

To eliminate any confusion, the ink binder resin is also referred to herein as the first binder resin to distinguish it from the second binder resin used to prepare the surface modified or coated colorant.

pH ADJUSTING AGENT

The ink composition of the present invention may in addition comprise a pH adjusting agent. Any suitable pH adjusting agent, acid or base, can be used so as to maintain the pH of the ink composition in the range of from about 6.0 to about 8.0, preferably in the range of from about 6.5 to about 7.5. If a base is necessary, any suitable base can be used. Examples of suitable bases include ammonium hydroxide, sodium hydroxide, potassium hydroxide, sodium bicarbonate, potassium bicarbonate, and ammonium bicarbonate. Although any suitable base can be used, it is preferred to make use of a base which can be eliminated by evaporation. Thus, it is preferable to use a base such as ammonium hydroxide for controlling the pH within the desired range.

Any suitable amount of the pH adjusting agent can be used. The pH adjusting agent is used preferably in an amount ranging from about 0.01% by weight to about 1.0% by weight of the ink composition.

HUMECTANT

The ink composition of the present invention may in addition comprise a humectant to prevent drying of the ink during the printing operation, as well as during storage of the ink. Humectants are hydrophilic solvents having high boiling points, preferably above 100°C, and more preferably in the range of from about 150°C to about 250°C. Any suitable humectant known to those of ordinary skill in the art can be used. An example of a suitable humectant is

glycerin.

Any suitable amount of the humectant can be used, preferably in an amount of from about 0.5% by weight to about 5% by weight of the ink composition, and more preferably in the amount of from about 1% by weight to about 3% by weight of the ink composition.

BIOCIDE

The ink composition of the present invention may in addition comprise a suitable biocide to prevent growth of bacteria, mould or fungus. Any suitable biocide can be used. DOWICIL™ 150, 200, and 75, benzoate salts, sorbate salts, and the like, methyl p-hydroxybenzoate (Methyl Paraben) and 6-acetoxy-2,2-dimethyl-1,3-dioxane (available as Giv Gard DXN from Givaudam Corp.) are examples of suitable biocides, with Methyl Paraben being a preferred biocide. The biocide can be present in the ink of the instant invention in an amount sufficient to prevent the attack by bacteria, mould, and fungus, which amount can be in the range of from about 0.05% by weight to about 0.5% by weight, preferably in the amount of from about 0.1% by weight of to about 0.3% by weight of the ink composition.

OTHER INGREDIENTS

The jet ink composition of the present invention may in addition comprise agents to optimize the properties and characteristics of the jet ink composition, for instance, to adjust the conductivity. If present, the conductivity adjusting agent should be present in an amount in the range of from about 0.1% to about 0.5% by weight of the ink composition. Examples of suitable agents to adjust conductivity include food grade ammonium, sodium, or potassium salts of organic acids, such as sodium acetate, potassium lactate, or sodium propionate.

The ink composition of the present invention may in addition comprise a defoamer to prevent foaming of the jet ink during its preparation, as well as during the printing operation. Any suitable defoamer known to those of

ordinary skill in the art can be used.

Suitable defoamers include silicone defoamers and acetylenic defoamers. Examples of commercially available defoamers include silicone defoamers, such as DC-150, which can be obtained from Dow Corning Co., and SILVET I-77, 720, 722, or 7002, which can be obtained from Union Carbide Co. A preferred defoamer is XRM-3588E™, which can be obtained from Ultra Additives Inc., in Paterson, New Jersey. XRM-3588E is a defoamer generally used in metal cutting fluids, and has a Brookfield (RVF Spindle #4, 20 RPM, 25°C) viscosity of 6,000 to 9,000 cps, a specific gravity of 0.984-1.032, and a pH of 7.0-8.5 (50% solution). The chemistry of XRM-3588E has not been published, and is believed to be a silicone defoamer.

Examples of acetylenic defoamers include the SURFYNOL™ brand defoamers which can be obtained from Air Products and Chemical Co. in Allentown, Pennsylvania. A number of Surfynol defoamers are available, including the preferred Surfynol 104 (2,4,7,9-tetramethyl-5-decyn-4,7-diol), which is available as a solution in a variety of solvents as Surfynol 104A, Surfynol 104E, Surfynol 104H, and Surfynol 104BC, and other Surfynols such as Surfynol GA, Surfynol SE, Surfynol TG, Surfynol PC, the dimethyl hexynediol, Surfynol 61, the dimethyl octynediol, Surfynol 82, the ethoxylated derivatives of the tetramethyl decynediol, Surfynol 440, Surfynol 465, and Surfynol 485, all of which can be used in the instant invention.

Any suitable amount effective to prevent foaming of the jet ink during preparation and use can be used, preferably an amount in the range of from about 0.01% by weight to about 1% by weight of the ink composition, and more preferably in the range of from about 0.05% by weight to about 0.35% by weight of the ink composition. The weight percentages given above refer to that of the active ingredient, and if the defoamer is sold in a diluted form, the amount of the diluted defoamer used will be proportionately increased.

The jet ink composition of the present invention can

be prepared by any suitable method, for instance, by combining and mixing the necessary ingredients. The jet ink is preferably prepared as follows. The solvent containing the required amounts of ethanol and water is prepared. The required amount of the base is added to adjust the pH to the desired level. The first binder resin is then dissolved in the above solution. The solution is then added to a stirred ink concentrate (surface modified or coated colorant) and mixing is continued until a well dispersed jet ink is obtained.

The following illustrative examples further illustrate the present invention but, of course, should not be construed as in any way limiting its scope.

## EXAMPLE 1

This example illustrates the preparation of a surface modified or coated colorant wherein the colorant is titanium dioxide.

2280 grams of the solvent (SDA 23 A 190 proof alcohol from Quantum Chemical Corp. in Cincinnati, Ohio) were taken in a container equipped with a high shear mixer and a temperature controller and kept at a temperature of about 40°C (±2°C). 720 grams of Certified R-49 refined bleached shellac resin were added slowly to the solvent while mixing was maintained. Upon complete dissolution, the solution was filtered through a sock filter of 5 microns pore size.

330 grams of the above solution were taken in a reaction vessel equipped with a high shear mixer and a temperature controller and maintained at a constant temperature of about 40°C. 80 grams of PLASDONE K-29/32 were added slowly over a period of about 20 minutes with slow mixing at a speed of about 500 rpm. After the mixture turned into a clear transparent solution, 40 grams of ETHOCEL Standard #4 Premium were added slowly over a period of about 20 minutes while maintaining the reaction vessel at about 40°C. The speed of mixing was increased to 1000 rpm and the mixing was maintained for about 5-10 minutes. 550 grams of KOWET titanium dioxide were added slowly and

continuously over a period of 15 minutes, and the contents were mixed at a high speed, of about 5,000 rpm, for about 30 minutes during which period the temperature of the vessel was maintained at about 40°C. The vessel was allowed to cool to ambient temperature and the resulting concentrate paste was recovered.

550 grams of the above concentrate paste were diluted with 50 grams of SDA-23A alcohol and ground in a horizontal bead mill using YTZ beads of size 0.8 mm in diameter for a period of 20 minutes at 5,000 rpm.

## EXAMPLE 2

This example illustrates the preparation of a jet ink composition of the present invention using the surface modified or coated titanium dioxide prepared as in Example 1. Shellac was used as the ink binder resin.

| MATERIALS | VENDORS | WEIGHT % |
|---|---|---|
| Confectioner's Dewaxed White Lac Glaze Four Pound cut in 200 proof | | |
| SDA-45 ethanol | Mantrose-Bradshaw | 20.64 |
| Ammonium Hydroxide (30%) | | 0.50 |
| CP-TS-38* | MICAP Technology | 17.00 |
| Deionized Water | | 10.00 |
| Pure Ethanol 200 Proof | Grain Processing | 51.86 |

* surface modified or coated titanium dioxide containing 9.4 g of $TiO_2$, 2.7 g of shellac, and 5.0 g of ethanol, prepared as in Example 1.

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The jet ink composition was prepared as follows.

Part A

Weighed amounts of ethanol and deionized water were taken in a container and mixed with a magnetic spin bar. The required amount of ammonium hydroxide was added and mixed for about 5 minutes. The required amount of Confectioner's Dewaxed White Lac Glaze Four Pound cut in 200 proof SDA-45 was added and mixed for about 15 minutes.

Part B

The required amount of the surface modified or coated colorant was placed in a clean stainless steel vessel and mixed in a high speed mixer at a speed of about 4000-5000 rpm. The blade of the mixer was maintained in the centre of the vessel to obtain uniform mixing. The mixed concentrate had the appearance of a doughnut in the high speed mixer. The solution obtained in Part A was added slowly to the ink concentrate keeping the contents continuously mixed. After the addition of the Part A solution was complete, the speed was increased to about 8000 rpm. The mixing was continued for one hour.

The resulting ink was filtered in two stages under vacuum. In the first stage, large particles were removed using a coarse filter. In the second stage, a five micron filter was used to remove particles larger than 5 microns. The resulting ink remained stable without phase separation.

## EXAMPLE 3

This Example illustrates the utility of the ink composition of the present invention in jet printing on glazed candies.

A laboratory scale jet printing head was mounted so as to direct a stream of ink droplets at a conveyor belt. A series of M&M candies was placed on an adhesive tape to be individually held thereby and the taped candies were anchored to the conveyor belt. As the conveyor belt transported the candies by the print head, each candy was jet printed with the inventive ink composition. Subsequent to printing, the elapsed time before complete drying was monitored using a stop watch. The ink drying time was less than one second. A high quality print was obtained. No smearing or smudging was found.

## EXAMPLE 4

This example illustrates the preparation of a jet ink composition of the present invention using the surface modified or coated colorant prepared as in Example 1. PVP

was used as the ink binder resin.

| MATERIALS | VENDORS | WEIGHT % |
|---|---|---|
| PLASDONE K29/32* | GAF Chemicals | 4.00 |
| Ammonium Hydroxide (30%) | | 0.50 |
| CP-TS-038** | MICAP Technology | 14.00 |
| Deionized Water | | 10.00 |
| Pure Ethanol 200 Proof | Grain Processing | 71.50 |

* poly(1-vinyl-2-pyrrolidone)

** surface modified or coated titanium dioxide containing 9.4 g of $TiO_2$, 2.7 g of shellac, and 5.0 g of ethanol, prepared as in Example 1.

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The above ingredients were combined to produce the jet ink composition following the procedure set forth in Example 2, except that PLASDONE K29/32 was used in place of the shellac solution.

The jet ink composition was successfully printed on M&M candies, as set forth in Example 3. The drying time was less than 1 second. No smudging or smearing of the print was observed.

The present invention provides a jet ink composition wherein the surface modified or coated colorant is present in the range of from about 10% by weight to about 20% by weight of the jet ink composition, the first binder resin is present in the range of from about 5% by weight to about 10% by weight of the jet ink composition, the first organic solvent is present in the range of from about 40% by weight to about 80% by weight of the jet ink composition, water is present in the range of from about 5% to about 15% by weight of the jet ink composition, and the pH adjusting agent is present in the range of from about 0.1% by weight to about 1% by weight of the jet ink composition.

The present invention further provides an improved process of jet ink printing on food and pharmaceutical articles, the improvement comprising using a jet ink composition having short drying times, comprising a first organic solvent, a first binder resin, and a surface modified or coated colorant, the surface modified or coated

colorant comprising a second binder resin such as shellac, a second organic solvent and an inorganic colorant having a mean particle size in the range of from about 0.01 microns to about 25 microns.

The present invention further provides an improved process of jet ink printing wherein the first organic solvent of the jet ink composition is ethanol. The present invention further provides an improved process of jet ink printing process wherein the first binder resin of the jet ink is selected from the group consisting of shellac and polyvinylpyrrolidone. The present invention further provides an improved process of jet ink printing wherein the modified or coated comprises titanium dioxide.

The present invention further provides an improved process of jet ink printing, wherein the surface modified or coated colorant comprises a second binder resin selected from the group consisting shellac, polyvinylpyrrolidone and ethylcellulose.

The present invention provides a jet ink composition comprising a first organic solvent, a first binder resin, and a surface modified or coated colorant, wherein the surface modified or coated colorant comprises shellac and an inorganic colorant having a mean particle size of from about 0.01 microns to about 25 microns, wherein the surface modified or coated colorant being prepared by a process comprising:

(a) dissolving from about 5 to about 35 parts by weight of shellac in about 20 to about 50 parts by weight of a second organic solvent; and

(b) dispersing from about 20 to about 60 parts by weight of the colorant in the solution obtained in step (a).

The present invention further provides a jet ink composition as set forth above, wherein the inorganic colorant is titanium dioxide.

The present invention further provides a jet ink composition as set forth above, wherein the second organic solvent is ethanol.

The present invention further provides a jet ink composition as set forth above, wherein the shellac is a refined bleached shellac.

The present invention further provides a jet ink composition as set forth above, further comprising the step of dissolving up to about 20 parts by weight of polyvinylpyrrolidone in the solution obtained by dissolving shellac in the second organic solvent.

The present invention further provides a jet ink composition as set forth above, wherein the polyvinylpyrrolidone has a viscosity average molecular weight in the range of from about 10,000 to about 360,000 Daltons.

The present invention further provides a jet ink composition as set forth above, further comprising the step of dissolving up to about 15 parts by weight of ethylcellulose in the solution obtained by dissolving shellac and polyvinylpyrrolidone in the second organic solvent.

The present invention further provides a jet ink composition as set forth above, wherein the ethylcellulose has a viscosity in the range of from about 3 cps to about 50 cps when measured as a 5% solution at 25°C in an Ubbelohde viscometer employing a solvent containing 80% toluene and 20% ethanol.

The present invention further provides a jet ink composition as set forth above, wherein the first organic solvent is an alcohol, preferably ethanol.

The present invention provides a jet ink composition as set forth above, wherein the first binder resin is selected from the group consisting of shellac and polyvinylpyrrolidone.

The present invention further provides a jet ink composition as set forth above, and further comprising water.

The present invention further provides a jet ink composition as set forth above, and further comprising a pH adjusting agent, for instance, ammonium hydroxide.

The present invention further provides a jet ink composition as set forth above, wherein the first binder resin is dewaxed shellac.

**CLAIMS**

1. A jet ink composition suitable for printing on food and pharmaceutical articles comprising a first organic solvent, a first binder resin, and a surface modified or coated colorant.

2. A jet ink composition as claimed in claim 1, wherein said surface modified or coated colorant comprises an inorganic colorant having a mean particle size in the range of from about 0.01 microns to about 25 microns, a second organic solvent, and one or more of second binder resins.

3. A jet ink composition as claimed in claim 2, wherein said second binder resin is selected from the group consisting of shellac, polyvinylpyrrolidone, and cellulose ethers such as methylcellulose and ethylcellulose.

4. A jet ink composition as claimed in claim 2 or 3, wherein said inorganic colorant is titanium dioxide.

5. A jet ink composition as claimed in claim 4, wherein said titanium dioxide is selected from the group consisting of anatase and rutile.

6. A jet ink composition as claimed in claim 5, wherein said titanium dioxide has a mean particle size in the range of from about 0.1 microns to about 2 microns.

7. A jet ink composition as claimed in any one of claims 2 to 6, wherein said second organic solvent is an alcohol.

8. A jet ink composition as claimed in any one of claims 2 to 7, wherein said shellac of said surface modified or coated colorant is a bleached shellac.

9. A jet ink composition as claimed in claim 8, wherein said shellac has an acid value in the range of 73-95 mg KOH/g, an ester value in the range of 150-180 mg KOH/g, a hydroxyl value in the range of 230-260 mg KOH/g, and an iodine value in the range of 7-12 decigram I/g.

10. A jet ink composition as claimed in any one of claims 2 to 7, wherein said cellulose ether is ethylcellulose having an ethoxyl content of from 45.0% to 49.5% by weight of said ethylcellulose.

11. A jet ink composition as claimed in claim 10, wherein said titanium dioxide is present in the range of from 20 to 60% by weight of said surface modified or coated colorant, said shellac is present in the range of from about 5% to about 35% by weight of said surface modified or coated colorant, said polyvinylpyrrolidone is present in the range of from above 0% to 20% by weight of said surface modified or coated colorant, said ethylcellulose is present in the range of from above 0% to 15% by weight of said surface modified or coated colorant, and said ethanol is present in the range of from 20% to 60% by weight of said surface modified or coated colorant.

12. A jet ink composition as claimed in claim 11, wherein said surface modified or coated colorant is prepared by a method comprising the steps of :

(a) dissolving said shellac in said ethanol;

(b) dissolving said polyvinylpyrrolidone in the solution obtained in step (a);

(c) dissolving said ethylcellulose in the solution obtained in step (b); and

(d) dispersing said titanium dioxide in the solution obtained in step (c).

13. A jet ink composition as claimed in any one of the preceding claims, wherein said first organic solvent is an alcohol.

14. A jet ink composition as claimed in any one of the preceding claims, wherein said first binder resin is selected from the group consisting of shellac and polyvinylpyrrolidone.

15. A jet ink composition as claimed in any one of the preceding claims, further comprising water.

16. A jet ink composition as claimed in any one of the preceding claims, further comprising a pH adjusting agent.

17. A jet ink composition as claimed in claim 14, 15 and 16, wherein said surface modified or coated colorant is present in the range of from 10% by weight to 20% by weight of the jet ink composition, said shellac is present in the range of from 5% by weight to 10% by weight of the jet ink composition, said first organic solvent is present in the range of from 40% by weight to 80% by weight of the jet ink composition, said water is present in the range of from 5% to 15% by weight of the jet ink composition, and said pH adjusting agent is present in the range of from 0.1% by weight to 1% by weight of the jet ink composition.

18. A jet ink composition as claimed in claims 14, 15 and 16, wherein said surface modified or coated colorant is present in the range of from 10% by weight to 20% by weight of the jet ink composition, said polyvinylpyrrolidone is present in the range of from 2% by weight to 6% by weight of the jet ink composition, said first organic solvent is present in the range of from 40% by weight to 80% by weight of the jet ink composition, said water is present in the

range of from 5% to 15% by weight of the jet ink composition, and said pH adjusting agent is present in the range of from 0.1% by weight to 1% by weight of the jet ink composition.

19. A jet ink composition as claimed in any one of claims 2 to 18, wherein said surface modified or coated colorant is prepared by a process comprising:

(a) dissolving from 5 to 35 parts by weight of said shellac in 20 to 50 parts by weight of a second organic solvent; and

(b) dispersing from 20 to 60 parts by weight of said colorant in the solution obtained in step (a).

20. A jet ink composition as claimed in claims 3 and 19, wherein said process further comprises the step of dissolving up to 20 parts by weight of polyvinylpyrrolidone in the solution obtained by dissolving shellac in said second organic solvent.

21. A jet ink composition as claimed in claim 20, further comprising the step of dissolving up to 15 parts by weight of ethylcellulose in the solution obtained by dissolving shellac and polyvinylpyrrolidone in said second organic solvent.

22. A jet ink composition as claimed in claims 19, 20 or 21, further comprising drying said surface modified or coated colorant to remove said second organic solvent.

## AMENDED CLAIMS

[received by the International Bureau on 11 April 1997 (11.04.97); original claims 4-11 and 17-20 amended; remaining claims unchanged (4 pages)]

1. A jet ink composition suitable for printing on food and pharmaceutical articles comprising a first organic solvent, a first binder resin, and a surface modified or coated colorant.

2. A jet ink composition as claimed in claim 1, wherein said surface modified or coated colorant comprises an inorganic colorant having a mean particle size in the range of from about 0.01 microns to about 25 microns, a second organic solvent, and one or more of second binder resins.

3. A jet ink composition as claimed in claim 2, wherein said second binder resin is selected from the group consisting of shellac, polyvinylpyrrolidone, and cellulose ethers such as methylcellulose and ethylcellulose.

4. A jet ink composition as claimed in claim 3, wherein said shellac of said surface modified or coated colorant is a bleached shellac.

5. A jet ink composition as claimed in claim 4, wherein said shellac has an acid value in the range of 73-95 mg KOH/g, an ester value in the range of 150-180 mg KOH/g, a hydroxyl value in the range of 230-260 mg KOH/g, and an iodine value in the range of 7-12 decigram I/g.

6. A jet ink composition as claimed in claim 3, wherein said cellulose ether is ethylcellulose having an ethoxyl content of from 45.0% to 49.5% by weight of said ethylcellulose.

7. A jet ink composition as claimed in any one of claims 2 to 6, wherein said inorganic colorant is titanium

dioxide.

8. A jet ink composition as claimed in claim 7, wherein said titanium dioxide is selected from the group consisting of anatase and rutile.

9. A jet ink composition as claimed in claim 8, wherein said titanium dioxide has a mean particle size in the range of from about 0.1 microns to about 2 microns.

10. A jet ink composition as claimed in any one of claims 2 to 9, wherein said second organic solvent is an alcohol such as ethanol.

11. A jet ink composition as claimed in claims 3, 8 and 10, wherein said titanium dioxide is present in the range of from 20 to 60% by weight of said surface modified or coated colorant, said shellac is present in the range of from about 5% to about 35% by weight of said surface modified or coated colorant, said polyvinylpyrrolidone is present in the range of from above 0% to 20% by weight of said surface modified or coated colorant, said ethylcellulose is present in the range of from above 0% to 15% by weight of said surface modified or coated colorant, and said ethanol is present in the range of from 20% to 60% by weight of said surface modified or coated colorant.

12. A jet ink composition as claimed in claim 11, wherein said surface modified or coated colorant is prepared by a method comprising the steps of :

(a) dissolving said shellac in said ethanol;

(b) dissolving said polyvinylpyrrolidone in the solution obtained in step (a);

(c) dissolving said ethylcellulose in the solution obtained in step (b); and

(d) dispersing said titanium dioxide in the solution obtained in step (c).

13. A jet ink composition as claimed in any one of the preceding claims, wherein said first organic solvent is an alcohol.

14. A jet ink composition as claimed in any one of the preceding claims, wherein said first binder resin is selected from the group consisting of shellac and polyvinylpyrrolidone.

15. A jet ink composition as claimed in any one of the preceding claims, further comprising water.

16. A jet ink composition as claimed in any one of the preceding claims, further comprising a pH adjusting agent.

17. A jet ink composition as claimed in claim 14, 15 and 16, wherein said surface modified or coated colorant is present in the range of from 10% by weight to 20% by weight of the jet ink composition, said first binder shellac resin is present in the range of from 5% by weight to 10% by weight of the jet ink composition, said first organic solvent is present in the range of from 40% by weight to 80% by weight of the jet ink composition, said water is present in the range of from 5% to 15% by weight of the jet ink composition, and said pH adjusting agent is present in the range of from 0.1% by weight to 1% by weight of the jet ink composition.

18. A jet ink composition as claimed in claims 14, 15 and 16, wherein said surface modified or coated colorant is present in the range of from 10% by weight to 20% by weight of the jet ink composition, said first binder

polyvinylpyrrolidone resin is present in the range of from 2% by weight to 6% by weight of the jet ink composition, said first organic solvent is present in the range of from 40% by weight to 80% by weight of the jet ink composition, said water is present in the range of from 5% to 15% by weight of the jet ink composition, and said pH adjusting agent is present in the range of from 0.1% by weight to 1% by weight of the jet ink composition.

19. A jet ink composition as claimed in any one of claims 4 to 18 when dependant upon claim 3, wherein said surface modified or coated colorant is prepared by a process comprising:

(a) dissolving from 5 to 35 parts by weight of said shellac in 20 to 50 parts by weight of said second organic solvent; and

(b) dispersing from 20 to 60 parts by weight of said colorant in the solution obtained in step (a).

20. A jet ink composition as claimed in claim 19, wherein said process further comprises the step of dissolving up to 20 parts by weight of polyvinylpyrrolidone in the solution obtained by dissolving shellac in said second organic solvent.

21. A jet ink composition as claimed in claim 20, further comprising the step of dissolving up to 15 parts by weight of ethylcellulose in the solution obtained by dissolving shellac and polyvinylpyrrolidone in said second organic solvent.

22. A jet ink composition as claimed in claims 19, 20 or 21, further comprising drying said surface modified or coated colorant to remove said second organic solvent.

# INTERNATIONAL SEARCH REPORT

Int· ·ional Application No
PC·/GB 96/02702

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | WO 95 01404 A (TONEJET) 12 January 1995<br>see page 3, line 30 - page 7, line 33;<br>claims 1-10; examples | 1 |
| A | GB 2 277 094 A (DOMINO PRINTING SCIENCES)<br>19 October 1994<br>see page 2, line 18 - page 5, line 29;<br>claims 1-6 | 1 |
| A | US 5 397 387 A (DENG ET AL ) 14 March 1995<br>see column 3, line 12 - column 6, line 24;<br>claims 1-6 | 1 |
| A | CH 662 358 A (BÜTTNER ET AL) 30 September 1987<br>see page 2, column 2, line 18 - page 4,<br>column 2, line 4; claims 1,4-10 | 1 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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1

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 6 March 1997 | 26.03.97 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. ( + 31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax ( + 31-70) 340-3016 | Bourgonje, A |

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter ·onal Application No
PC1/GB 96/02702

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